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(54) Compositions containing EP additives for the metal-working industry

(57) A coolant-lubricating liquid composition containing organic polysulphides and usable in cutting and non-cutting cool-shaping of metals, mainly steel alloys, comprises an organic polysulphide of the general formula (I),

$$(R^{I-V}-Ar_b)_c(S_x)_d \qquad (I)$$

wherein R^I, R^{II} . . . R^V are the same or different and each stands for a hydrogen atom, a C_{1-40} straight brached chain or cyclic saturated and/or unsaturated hydrocarbyl group and/or a derivative thereof; Ar stands for a monocyclic and/or polycyclic aromatic hydrocarbyl group and/or a derivative thereof; b is an integer from 0 to 5; c is an integer from 2 to 10; d is an integer from 1 to 9; and x is an integer from 1 to 6.

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SPECIFICATION

Compositions containing EP additives for the metal-working industry

The invention relates to coolant-lubricating compositions containing organic polysulphides and usable in cutting and non-cutting cool-shaping of metals, mainly steel alloys.

It is known that the coolant-lubricating fluids used in cutting, drilling and holing cool-shaping of metals, carried out on modern high speed metal-working machines, have to simultaneously satisfy several high standard needs. On using them, the tool must not display any superficial pitting or striation, they may not result in the formation of any polluting layer on the worked metal-surface, and they have to ensure temporary protective action against corrosion.

A wide range of coolant-lubricating additives is known, as among others natural and synthetic oils with or without additives and the aqueous emulsions thereof, as well as other semi-synthetic and synthetic materials.

The effectivity of the different materials in use is varying from the view-points of cooling effect, layer-diminishing, wear-diminishing and effect on the environment, and neither of them is able to simultaneously ensure a total solution in all respects. Among the above-mentioned material systems of materials the oils containing additives and the aqueous emulsions thereof are most important and widespread. The additive oils are oils of vegetable or mineral origin and combinations thereof, frequently containing chlorine, nitrogen and phosphorus compounds, and the combinations thereof, respectively, as well as solid additives, e.g. molybdenum sulphide or graphite as EP-extreme pressure-additives. The EP additives are first of all needed in high-speed cutting working, where lubrication has to be ensured because of high pressure and mainly because of high surface temperature.

The aim of the present invention is to ensure a set of coolant-lubricating products suitable for any operation in the working of hard metals, as for cutting, more precisely turning, drilling, grinding, holing as well as for cool non-cutting working, more precisely pressing and deep-drawing.

The invention is based on the recognition that the above aim can be attained by using an EP additive of organic polysulphides, containing active sulphur, prepared according to the published Hungarian applications Nos. 2268/85 and 2269/85, of the general formula,

$$/R^{I\ V}-Ar_b/_c\ /S_x/_d \qquad (I)$$

wherein R^I, R^{II} ... R^V are the same or different, and each represents a hydrogen atom, a C_{1-40} straight or branched chain or cyclic, saturated and/or unsaturated hydrocarbyl group and/or a derivative thereof, A, represents a mono- and/or polycyclic aromatic hydrocarbyl group and/or a derivative thereof,

b is an integer from 0 to 5,

c is an integer from 2 to 10,

d is an integer from 1 to 9, and

x is an integer from 1 to 6,

which can be prepared by the reaction of sodium-polysulphide and alkylaromatic compounds containing halogens, and which are constituted at least to one third part by mass by polysulphides of the general formula (I) wherein c stands for an integer of at least 3, d stands for an integer of at least 2 and x represents an integer from 2 to 6.

The sulphur content of the thus-prepared polysulphide varies from 30 to 50 % by mass, and at least 40 % by mass of the total sulphur content is active, that is able to go into reaction with metal copper according to the standard method ASTM D-1662.

Sulphurated hydrocarbons suitable for manufacturing EP additives are prepared in high quantities e.g. by direct sulphuration of unsaturated compounds under high pressures and at high temperature (US-P Nos. 4,119,560, 4,119,549, 3,221,056 and 3,419,614; GE-P No. 2,838,981). In these processes generally C_{3-6} olefines, mainly isobutylene, diisobutylene and triisobutylene, are sulphurized, whereby products of general formula (II) are obtained,

$$R^{I-III}C-(S)_x-CR^{I-III} \qquad (II)$$

wherein R^I, R^{II} and R^{III} are the same or different and each stands for hydrogen atom, a C_{3-31} (generally lower than C_7) alkyl, alkenyl or aryl group and a derivative thereof and X is mainly an integer from 1 to 3.

The welding load of a ditert-butyl-polysulphide, containing 38 % by mass of sulphur and prepared according to GE-P No. 2,838,981 by sulphurizing isobutylene, at a concentration of 6.5 % by mass in a machine oil fraction having a flash point of 168 °C, amounts to 4000 N, measured by the method of standard DIN 51,350. On the other hand, the polysulphide having the general formula (I) gives in the same basic oil a welding load of 6500 N at a concentration

of 6.5 % by mass and 4000 N at a concentration of 3.5 % by mass.

We have recognized that the advantageous EP effect is ensured by the organic group, mainly the structure of the sulphur-containing organic compound, and not by the absolute amount of the built-in sulphur.

Based on the above, the invention relates to a coolant-lubricating liquid composition containing organic polysulphides and usable in cutting and non-cutting cool-shaping of metals, mainly steel alloys, comprising

2 to 8 % by mass of an organic polysulphide of the general formula (I),

$$(R^{I-V}-Ar_b)_c(S_x)_d \qquad (I)$$

wherein

R^I, R^{II} ... R^V are the same or different and each stands for a hydrogen atom, a C_{1-40} straight or branched chain or cyclic saturated and/or unsaturated hydrocarbyl group and/or a derivative thereof;

Ar stands for a monocyclic and/or polycyclic aromatic hydrocarbyl group and/or a derivative thereof;

b is an integer from 0 to 5;

c is an integer from 2 to 10;

d is an integer from 1 to 9; and

x is an integer from 1 to 6;

with the proviso that at least one third part by mass of the said organic polysulphide is a compound of the general formula (I) wherein c is at least 3, d is at least 2, x is an integer from 2 to 6 and at least 40 % of the total sulphur content are active,

3 to 12.5 % by mass of an emulsifier of detergment effect and/or

0.5 to 15 % by mass of a lubrication-improving and viscosity-modifying additive,

0.5 to 1.5 % by mass of a corrosion-inhibitor,

63 to 94 % by mass of a hydrocarbon distillate or a solvent of chlorinated hydrocarbon basis as carrier and, if desired, on the account of the carrier solvent,

0.1 to 0.3 % by mass of oxydation inhibitor,

0.01 to 0.5 % by mass of biocide additive,

0.01 to 0.1 % by mass of an organic dyestuff and

0.2 to 1.0 % by mass of an aromatic agent.

With the aid of these compositions auxiliary materials for the metal-working industry are obtained that can be widely used directly or diluted with 5 to 95 % by mass of water for cutting and non-cutting cool-shaping of metals.

The composition of the invention contains preferably the following components as lubrication-improving and viscosity-modifying additives: mono- and triglycerides, methylesters, epoxidized and ethoxylated esters of various natural, mainly vegetable, oils, fatty acids, chlorinated paraffins with a chlorine content of 40 to 70 % by mass, stearine monoglyceride, polycetylmethacrylate, polyisobutylene or chlorinated or chloromethylated polyethylene or polypropylene.

As washing, rinsing and emulsifier additives preferably adducts of a fatty alcohol and ethylene oxide, sodium salts of alkylbenzenesulphonic acids, alkylphenol-polyethyleneglycolethers, oxyethylated fatty amides, modified fatty amine salts of organic acids containing nitrogen and butyldiglycol can be used.

As corrosion inhibitors fatty imidazole derivatives, N-acyl-sarcosine, fatty sarcosine, dicyclohexylamine, N-2-phenylnaphthalene and triethanolamine oleate can be used.

The carrier mineral oil distillate does not need any oxidation inhibitor since the organic polysulphide contains active sulphur which is transformed at higher temperatures to tetra- and hexavalent sulphur of oxygen-acceptor character.

Compounds of phenolic character such as 2,6-tert-butyl-p-cresol, alkylated dimethylamine-tert-butylphenol, triethyleneglycol-bis-propionate, further organic nitrogen compounds such as phenyl-2-naphthylamine can advantageously used for inhibiting the esters of natural fatty acids.

As biocide additives cetyl-pyridinium-chloride, cetyl-pyridinium-bromide or trimethoxynitromethane can preferably be used.

Turpentine oil and benzaldehyde can be advantageously used as aromatic agent whereas monoazo- or phthalocyanine-type dyes soluble in fats and alcohols can be used as organic dyestuff.

Beside the polysulfide ensuring lubricating effect and additives, the hydrocarbon-type solvent or its aqueous emulsion is mainly a carrier but it ensures also the cooling-rinsing effect and the heat-withdrawal. The following hydrocarbon fractions were chosen as carriers:

I. *Aromatic light gas-oil fraction*

Boiling point limit	200–280 °C
Viscosity at 50 °C	1.5–2.7 mm²/s
Flash point (Marcusson)	80–100 °C
Aromatic content	15–35 °C

II. *Naphtenic oil distillate*

Viscosity at 50 °C	6–10 mm²/s
Flash point (Marcusson)	140–180 °C
Point of solidification	below −40 °C
Number of carbon atoms in naphthenic bond	at least 30 %

III. *Spindle oil or vaseline oil*

viscosity at 50 °C	8–15 mm²/s
Flash point (Marcusson)	at least 150 °C
Point of solidification	at most 8 °C

IV. *Machine oil fraction*

Viscosity at 50 °C	15–50 mm²/s
Flash point (Marcusson)	150–200 °C
Point of solidification	at most −10 °C

V. *Heavy oil fraction*

Viscosity at 50 °C	50–120 mm²/s
Flash point (Marcusson)	at least 200 °C
Point of solidification	−15 to −25 °C

VI. *Residue oil*

Viscosity at 50 °C	at least 120 mm²/s
Flash point (Marcusson)	above 240 °C
Point of solidification	−8 to −18 °C

From the mineral oil derivatives those having a viscosity exceeding 8 mm²/s at 50 °C can be used as carriers independently from their composition.

The C_{1-6} hydrocarbons halogenated to various extents, such as dichloroethane, carbon tetrachloride, trichloroethylene, hexachlorobutadiene or the mixtures thereof can be used as chlorinated solvents.

The usability of the compositions according to the invention in a wide range is rendered possible by the further recognition that the selected organic polysulphide exerts its excellent EP property in all the enumerated solvents. Furthermore it has been recognized that this excellent EP property is enhanced in a surprising degree by the employed detergents, so mainly by the ethylene oxide adducts of fatty acid esters and fatty alcohols, further by the employed lubrication-improving additives, mainly by the methylesters of epoxidized or ethoxylated vegetable oils. This synergism is shown with the aid of the following model mixtures:

Aromatic light gas oil fraction	100%
Four-ball welding load	1200N

Aromatic light gas oil fraction	97%
Organic polysulphide	3%
Four-ball welding load	4000N

Aromatic light gas oil fraction	90%
Ethyleneoxide adduct of fatty acids	10%
Four-ball welding load	2000N

Aromatic light gas oil fraction	87%
Organic polysulphide	3%
Ethyleneoxide adduct of fatty acids	10%
Four-ball welding load	8000N

The composition according to the invention is further illustrated by the following non-limiting Examples.

Example A	
Organic polysulphide	5%
Ethyleneoxide adduct of fatty acids	8%
Imidazole derivative of fatty acids	1%
Aromatic light gas oil fraction	84.99 %
Organic dyestuff of monoazo type	0.01 %
Turpentine oil	1%
Viscosity at 50 °C	4.2 mm^2/s
Flash point (Marcusson)	92°C
Four-ball welding load	8000N
Corrosion at 100 °C, 3 hours, on steel	negative
Example B	
Organic polysulphide	6%
Ethyleneoxide adduct of fatty acids	6%
Methylester of mixed vegetable oils	15%
Butyldiglycol	9%
Imidazole derivative of fatty acids	1%
Aromatic light gas oil fraction	62.6 %
Organic dyestuff of phthalo-cyanine type	0.1 %
Benzaldehyde	0.2 %
Triethyleneglycol-bispropionate	0.1 %
Viscosity at 50 °C	4.8 mm^2/S
Flash point (Marcusson)	107°C
Four-ball welding load	10000N
Corrosion at 100 °C, 3 hours, on steel	negative
Example C	
Organic polysulphide	6%
Ethyleneoxide adduct of fatty acids	6%
Methylester of mixed vegetable oils	10%
Imidazole derivative of fatty acids	1%
1,1,1-Trichloroethylene	77%
Viscosity at 50 °C	3.4 mm^2/S
Four-ball welding load	3000N
Corrosion at 100 °C, 3 hours, on steel	negative
Example D	
Organic polysulphide	2%
Ethyleneoxide adduct of fatty acids	3%
Chloroparaffin, 70 %, liquid	10%
Imidazole derivative of fatty acids	1%
1:1 mixture of dichloroethane and hexachlorobutadiene	86%
Viscosity at 50 °C	8.4 mm^2/s
Four-ball welding load	6000N
Corrosion at 100 °C, 3 hours, on steel	negative

Example E	
Organic polysulphide	3%
Sodium salt of alkylbenzene-sulfonic acid	5%
Epoxidized sunflower oil	12.5 %
N-Acyl-sarcosine	0.5 %
Naphthenic oil distillate	79%
Viscosity at 50 °C	6.3 mm^2/s
Flash point (Marcusson)	153°C
Four-ball welding load	8000N
Corrosion at 100 °C, 3 hours, on steel	negative
Example F	
Organic polysulphide	5%
Alkylphenyl-polyethyleneglycol ether	12.5 %
Methylester of sunflower oil	15%
Dicyclohexylamine	0.5 %
Spindle oil	76.7 %
2,6-tert-Butyl-p-cresol	0.3 %
Cetyl-pyridinium-chloride	0.5 %
Viscosity at 50 °C	12 mm^2/s
Flash point (Marcusson)	160°C
Four-ball welding load	5000N
Corrosion at 100 °C, 3 hours, on steel	negative
5 % aqueous emulsion	
Four-ball welding load	2000N
pH	8.0
Corrosion on cast iron turnings	corrosion grade 1
Example G	
Organic polysulphide	4%
Alkylphenol-polyethyleneglycol ether	8.5 %
Polycetyl-methacrylate	8%
Triethanolamine oleate	1.5 %
Vaseline oil	78%
Viscosity at 50 °C	22 mm^2/s
Flash point (Marcusson)	155°C
Four-ball welding load	6000N
Corrosion at 100 °C, 3 hours, on steel	negative
Example H	
Organic polysulphide	2%
Oxyethylated fatty acid amide	3%
Fatty acid sarcosine	1%
Machine oil fraction	94%
Viscosity at 50 °C	27 mm^2/s
Flash point (Marcusson)	170°C
Four-ball welding load	4000N
Corrosion at 100 °C, 3 hours, on steel	negative

Example I	
Organic polysulphide	3%
Ethyleneoxide adduct of fatty acids	5%
Chloroparaffin	8%
Polyisobutylene	3%
Dicyclohexylamine	1%
Refined heavy oil	80%
Viscosity at 50 °C	80 mm^2/s
Flash point (Marcusson)	224°C
Four-ball welding load	7000N
Corrosion at 100 °C, 3 hours, on steel	negative
Example J	
Organic polysylphide	7%
Alkylphenol-polyethyleneglycol ether	7.25 %
Chloroparaffin, 70 %	7%
Rape-seed oil	15%
N-2-Phenyl-naphthylamine	0.5 %
Refined heavy oil	63%
Tert-butyl-phenol	0.15 %
Trimethoxy-nitromethane	0.1 %
Viscosity at 50 °C	96 mm^2/s
Flash point (Marcusson)	226°C
Four-ball welding load	10000N
Corrosion at 100 °C, 3 hours, on steel	negative
10% aqueous emulsion	
Four-ball welding load	5000N
pH	8.0
Corrosion on cast iron turnings	corrosion grade 1
5% aqueous emulsion	
Four-ball welding load	3500N
Example K	
Organic polysulphide	6%
Ethyleneoxide adduct of fatty acids	12%
Stearine monoglyceride	10%
Triethanolamine oleate	1%
Refined residue oil	69%
Viscosity at 50 °C	132 mm^2/s
Flash point (Marcusson)	265°C
Four-ball welding load above 11000	N
Corrosion at 100 °C, 3 hours, on steel	negative
5 % aqueous emulsion	
Four-ball welding load	5500N
Corrosion on cast iron turnings	corrosion grade 1

Example L

Organic polysulphide	3%
Ethyleneoxide adduct of fatty acids	3%
Chlorinated polyethylene wax	5.5 %
Fatty acid sarcosine	0.5 %
Refined residue oil	88%
Viscosity at 50 °C	122 mm^2/s
Flash point (Marcusson)	155°C
Four-ball welding load above 8000	N
Corrosion at 100 °C, 3 hours, on steel	negative

The wide range of usability of the composition according to the invention is illustrated by the following two Tables.

Table I

Compositions for cutting

	Steel of medium strength	Rust-proof steel	Non-ferrous metals
Turning	Example A	Example A Example F 5 % aqueous emulsion	Example B Example C
Boring	Example A Example B Example C	Example A Example B	Example A Example B Example C Example D
Grinding	Example D	Example F 5 % aqueous emulsion Example J 5 % aqueous emulsion	Example E
Holing	Example A Example B	Example A Example B	Example A Example B

Table II

Compositions for non-cutting

	Steel of medium strength	Rust-proof steel	Non-ferrous metals
Wire drawing	Example E	Example G	Example F
Rolling	Example E Example G	Example J	Example E Example F Example G
Punching	Example J	Example J	Example E Example F Example G
Deep-drawing	Example K Example L	Example K Example L	Example I

CLAIMS

1. A coolant-lubricant liquid composition containing organic polysulphides and usable in cutting and non-cutting cool-shaping of metals, mainly steel alloys, comprising
2 to 8 % by mass of an organic polysulphide of the general formula (I)

$$(R^{I-V}-Ar_b)_c(S_x)_d \quad (I)$$

wherein
R^I, R^{II} ... R^V are the same or different and each stands for a hydrogen atom, a C_{1-40} straight or branched chain or cyclic saturated and/or unsaturated hydrocarbyl group and/or a derivative thereof;
Ar stands for a monocyclic and/or polycyclic aromatic hydrocarbyl group and/or a derivative thereof;
b is an integer from 0 to 5;
c is an integer from 2 to 10;
d is an integer from 1 to 9; and
x is an integer from 1 to 6;
with the proviso that at least one third part by mass of the said organic polysulphide is a compound of the general formula (I) wherein c is at least 3, d is at least 2, x is an integer from 2 to 6 and at least 40% of the total sulphur content are active,
at least 3 % mass of an emulsifier of detergent effect and/or
0 to 25% by mass of a lubrication-improving and viscosity-modifying additive,
0.5 to 1.5 % by mass of a corrosion-inhibitor, 60 to 94% by mass of a hydrocarbon distillate or a solvent of chlorinated hydrocarbon basis as carrier and, if desired, on the account of the carrier solvent,
0 to 0.3 % by mass of oxidation inhibitor,
0 to 0.5 % by mass of biocide additive,
0 to 0.1 % by mass of an organic dyestuff and
0 to 1.0 % by mass of an aromatic agent.

2. A composition as claimed in claim 1, which comprises as carrier a mineral oil fraction, having a flash point above 80 to 240 °C, and a viscosity above 1.5 to 120 mm^2/s at 50 °C, or chlorinated C_{1-6} hydrocarbons.

3. A composition as claimed in claim 1, which comprises as emulsifier adducts of a fatty alcohol and ethylene oxide, sodium salts of alkylbenzenesulphonic acids, alkylphenol-polyethyleneglycolethers, oxyethylated fatty amides and/or butyldiglycol.

4. A composition as claimed in claim 1, which comprises as lubrication-improving and viscosity-modifying additive a refined or epoxidized rape or sunflower oil and/or the methylester thereof, chlorinated paraffins with a chlorine content of 40 to 70 % by mass, stearine monoglyceride, polycetylmethacrylate, polyisobutylene or chlorinated or chloromethylated polyethylene or polypropylene.

5. A composition as claimed in claim 1, which comprises as corrosion inhibitor fatty imidazole derivatives, N-acyl-sarcosine, fatty sarcosine, dicyclohexylamine, N-2-phenylnaphthalene and/or triethanolamine oleate.

6. A composition as claimed in claim 1, which comprises as oxidation inhibitor 2,6-butylcresol, alkylated dimethylamine-tert-butylphenol, triethyleneglycol-bis-propionate and/or phenyl-2-naphthalene.

7. A composition as claimed in claim 1, which comprises as biocide additive cetyl-pyridinium-chloride, cetyl-pyridinium-bromide or trimethoxy-nitromethane.

8. A composition as claimed in claim 1, which comprises turpentine oil or benzaldehyde as aromatic agent.

9. A composition as claimed in claim 1, which comprises as organic dyestuff monoazo- or phthalocyanine-type dyes soluble in fats and alcohols.

10. A composition as claimed in any one of claims 1 to 9, which includes not more than 12.5% by weight of an emulsifier of detergent effect.

11. A composition as claimed in any one of claims 1 to 10, which includes at least 0.5% by weight of lubrication-improving and viscosity modifying additive.

12. A composition as claimed in claim 11, which includes not more than 15% by weight of the lubrication-improving and viscosity modifying additive.

13. A composition as claimed in any one of claims 1 to 12, which includes at least 63% by weight of the hydrocarbon distillate and/or a chlorinated hydrocarbon solvent.

14. A composition as claimed in any one of claims 1 to 13, which includes at least 0.1% by weight of an oxidation inhibitor.

15. A composition as claimed in any one of claims 1 to 14, which includes at least 0.01% by weight of a biocide.

16. A composition as claimed in any one of claims 1 to 15, which includes at least 0.01%

by weight of an organic dyestuff.

17. A composition as claimed in any one of claims 1 to 16, which includes at least 0.2% by weight of a perfume.

18. Compositions A to L as hereinbefore described.

19. Emulsions of the compositions as claimed in any one of claims 1 to 17 with 5 to 95% by weight water.

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